

AD A027 787

TECHNICAL REPORT

76-16 FEL

INVESTIGATION AND DEVELOPMENT OF AIR FOAM CUSHIONING

Monsanto Research Corporation
Dayton, Ohio 45407

Project Reference: 1T762713D552

July 1976

Approved for public release;
distribution unlimited.

UNITED STATES ARMY
NATICK RESEARCH and DEVELOPMENT COMMAND
NATICK, MASSACHUSETTS 01760



Food Engineering Laboratory
FEL-41

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 76-16 FEL	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) INVESTIGATION AND DEVELOPMENT OF AIR FOAM CUSHIONING		5. TYPE OF REPORT & PERIOD COVERED Final June 1974 - June 1975
		6. PERFORMING ORG. REPORT NUMBER FEL-41
7. AUTHOR(s) J. L. Schwendeman, S. M. Sun, T. G. Duffy, I. O. Salyer, C. L. Church, C. E. McClung		8. CONTRACT OR GRANT NUMBER(s) DAAK03-74-C-0178
9. PERFORMING ORGANIZATION NAME AND ADDRESS Monsanto Research Corporation Dayton, Ohio 45407		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1T762713D552 6.2 10
11. CONTROLLING OFFICE NAME AND ADDRESS US Army Natick Research and Development Command Natick, MA 01760		12. REPORT DATE June 1975
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 68 69
		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
CUSHIONING MATERIALS	PACKAGING MATERIALS	POLYURETHANE FOAM
CUSHIONING	SOLUTIONS (AQUEOUS)	POLYMERS
FOAMING	PLASTIC FOAM	LOGISTICS
GELATINS	CELLULAR PLASTICS	POLYSTYRENE
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>Monsanto Research Corporation investigated several water-soluble polymers, especially gelatin, to develop a foam cushioning technique that could be generated on site and that would be non-toxic.</p> <p>Gelatin solutions containing 10 to 40% gelatin could be processed into water soluble foam in an Oakes Mixer. This froth foam could be produced by pour-in-place method or could be made into pre-formed and cut ribbon</p>		

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

shapes. Sample gelatin foams exhibited high compression set. A sample of gelatin foam was compressed to 22% of its original thickness for 17 hours. The foam did not recover after the weight was removed.

Work on the foaming of polyvinyl alcohol solution with an Oakes Mixer produced a spongy, water soluble foam in limited quantities. It was necessary to stabilize the PVA foam by crosslinking it with resorcinol. PVA foams cured with resorcinol set up at the same rate as gelatin which is approximately 3 hours after being made. PVA foams, when compressed to 27% of their original thickness for 17 hours, recovered 66% of their original thickness immediately upon removal of the weight. After one hour, recovery is 90% of the original thickness.

Urea/formaldehyde foams were prepared using a commercial foaming process. These foams were not soluble when immersed in water for 24 hours. UF foams were also prepared which contained percentages of gelatin or PVA. Despite the presence of these water-soluble polymers, the UF foams did not break up when immersed in water.

ACCESSION NO.	
PTIC	<input checked="" type="checkbox"/>
EDS	<input type="checkbox"/>
PTIC	<input type="checkbox"/>
EDS	<input type="checkbox"/>
BY DATE	
A	

1a

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

PREFACE

Increased use of foam-in-place plastics for cushioning materials by various DoD Agencies has resulted in a disposal problem, particularly at supply centers or depots, and aboard ships at sea. Monsanto Research Corporation proposed to develop a foam cushioning material that could be generated on site at warehouses, depots, or aboard ships, and that would be non-toxic and water soluble. Subsequently, US Army Natick Research and Development Command, formerly the US Army Natick Development Center, contracted with Monsanto Research Corporation to investigate several water-soluble polymers, especially gelatin, in foam form. Foaming techniques were established and the standard product parameters of the foams produced were determined.

The project was carried out by the Monsanto Research Corporation's Dayton Laboratory, Dayton, Ohio. The project Leader was Mr. James L. Schwendeman. Project Officer for the US Army Natick Research and Development Command was Mr. Raymond T. Mansur of the Food Packaging Division, Food Engineering Laboratory and the Alternate Project Officer was Mr. Charles F. Macy of the Pollution Abatement Division, Food Sciences Laboratory.

TABLE OF CONTENTS

	<u>Page</u>
1. SUMMARY	7
2. TECHNICAL DISCUSSION	11
2.1 INTRODUCTION	11
2.2 MATERIALS AND EQUIPMENT	13
2.3 GELATIN FOAM DEVELOPMENT	13
2.3.1 Preparation of Gelatin Solutions	19
2.3.2 Evaluation of Foaming Processes	20
2.3.2.1 Approaches to Foam Formulation	20
2.3.2.2 Perspective on Pour-in-Place Foam Production	20
2.3.3 Water-Base High Expansion Foams	23
2.3.4 Foams from Gelatin Containing a Minimum Amount of Water	25
2.3.4.1 Use of Laboratory-Scale Z-Blade Mixer	26
2.3.4.2 Use of One-Inch Extruder	28
2.3.4.3 Use of One-Ounce Injection Molding Machine	30
2.3.4.4 Foaming of Strand by Use of Heat	32
2.3.5 Use of 20-50% Polymer Solutions	34
2.3.5.1 Use of the Oakes Mixer	34
a. Cost Estimates	
b. Gelatin Foam Properties	
2.3.5.2 Use of the UFC Mixer	48
a. Gelatin Froth Foams	
b. Urea/Formaldehyde Foams	
c. Urea/Formaldehyde Foam Containing Gelatin or Polyvinyl Alcohol	

TABLE OF CONTENTS

	<u>Page</u>
2.3.5.3 Miscellaneous Methods	56
a. Floatation Process	
b. Gelatin/Ethylene Glycol Solutions	
c. Production of Foam Beads Using a Spray Drying Technique	
d. Foams Produced from Gelled Solutions	
2.4 NON-AQUEOUS SOLVENT-BLOWN FOAMS	60
2.5 OTHER WATER-SOLUBLE POLYMERS	62
3. CONCLUSIONS	64
4. RECOMMENDATIONS	66

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.	Environmentally Degradable Foam Production	21
2.	Schematic Drawing of the Foam Generator	24
3.	Preparation of Foams from Highly Concentrated Polymer (Gelatin) Solution	27
4.	Diagram of Plastic Extruder	28
5.	Schematic of Injection Molding Machine	31
6.	Production of Foam From Low and Intermediate Concentration Polymer (Gelatin) Solutions	35
7.	Schematic of Oakes Mixer	36
8.	Oakes Mixer and Associated Equipment	37
9.	Interior of Oakes Mixer Head	39
10.	Overall View of UFC Foam Generator	49
11.	UF Foam Generator Head	50
12.	SideView of Foamed-Up Samples	61

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Metric Conversions	14
2	Materials Used	15, 16, 17
3	Equipment Used	18
4	Viscosity (Cp) of Aqueous Solutions of Three Water-Soluble Polymers	22
5	Compression Properties of Gelatin and Polyvinyl Alcohol Foams	64

INVESTIGATION AND DEVELOPMENT OF AIR FOAM CUSHIONING

1. SUMMARY

The objective of this study was to develop a new foam cushioning material that:

- (1) can be generated at warehouses, posts, or field centers for improved logistics;
- (2) does not present health or safety hazards during processing; and
- (3) can be disposed of after use without adverse effects on the environment.

Gelatin was selected as the prototype material for this study. High molecular weight gelatin (275 Bloom strength*) was chiefly used to obtain high strength foam. Various kinds of foaming agents, foaming processes, and foaming equipment were evaluated.

The most promising results were obtained using an Oakes mixer to prepare gelatin foam blocks (each over 1 cu ft) and a large quantity of gelatin foam "pillows". In making the foam blocks, water solutions containing either 40% Wilson 14X or Swift 610

*Bloom strength is a measure of jelly strength, peculiar to the gelatin industry. It is a measure of the depth of penetration of a cylindrical plunger into a block of gelatin of specified concentration.

gelatin and 20% glycerine were used. These solutions contained 0.01% sodium pentachlorophenate as a preservative. A proprietary foaming agent was used in these foams, and either compressed nitrogen or chlorofluorocarbon was used as a frothing or blowing agent. The nitrogen-blown foam had uniformly small cell size. For making foam "pillows", solutions containing either 30% 14X or 610 gelatin and 15% glycerine or 10% 14X or 610 gelatin and 5% glycerine were blown with nitrogen. Rods of these foams were laid down on kraft paper and later cut into small "pillows" which could serve as a pour-in packing material.

Samples cut from the gelatin foam blocks had the following properties:

Tensile Test (ASTM D2406)

Ultimate Strength	9.8 psi
Ultimate Elongation	164%

Compression Test (ASTM D1621)

Compression Strength:	10% Compression	11 psi
	60% Compression	24 psi

Compression Set

A sample of gelatin foam was compressed to 22% of its original thickness and left in that condition for 17 hours. This sample of foam did not recover after the weight was removed from the foam. One hour after removal the thickness was still 22% of the original dimension.

Moisture Adsorption Test (ASTM D2842)

After 2 hours	250%
After 24 hours	Mostly disintegrated

This test was conducted using deaerated distilled water. Saline water was not used in this test.

Flammability Test (ASTM D1692)

Burning Rate	1.85 inch/min.
Extinguishment Time	82 sec.
Self-extinguishing	2.5 inch burned in 82 sec.

Thermoconductivity (ASTM D2326)

0.20 Btu · in./ft² · hr · °F

Water Vapor Transmission (WVT) (ASTM C355)

WVT	350 g/24 hr · m ²
Permeance	0.332 metric perms
Permeability	0.652 metric perm-cm

Gelatin foams were exposed to 90-100% relative humidity with the following results.

Foam made from 20-30% gelatin solution - no apparent change.

Foam made from 10% solution was deformed and sticky.

Foam pillows adhered to each other.

At the end of the program, approximately 10 cu ft of gelatin foam blocks and 10 cu ft of gelatin foam pillows were prepared for evaluation by the Army.

Preliminary work on the foaming of polyvinyl alcohol solution with an Oakes mixer produced spongy foam in limited quantities. It was necessary to stabilize this foam by crosslinking it with resorcinol. Several promising foaming processes based on extrusion and injection molding were also developed, but only very limited quantities of foam samples could be obtained.

These polyvinyl alcohol foams are less expensive than are gelatin foams (\$0.94/lb vs \$2.33/lb). Polyvinyl alcohol foams cured with resorcinol set up at the same rate as does gelatin. Polyvinyl alcohol foams, when compressed to 27% of their original thickness and left for 17 hours in that condition, recover 66% of their original

thickness immediately when the weight is removed. After one hour, recovery is 90% of the original thickness.

Urea/formaldehyde foams were prepared using a commercial process. These foams were not destroyed by immersion in water, weak acids, or bases. There was slight evidence of microbial attack on these foams. Urea/formaldehydes were also prepared which contained gelatin or polyvinyl alcohol. Despite the presence of these water-soluble polymers, the urea/formaldehyde foam remained intact after immersion in water.

2. TECHNICAL DISCUSSION

2.1 INTRODUCTION

Conventional materials used for packaging applications consist of a variety of individual materials and composite structures such as wood shavings, crepe paper, sponge, and honeycomb structures. These materials are used for specific packaging functions. One function is to cushion the article from impact. In certain applications, the cushioning material can be applied directly to encapsulate the article. In other uses it can be placed around the article to fill the empty space in the container.

Many types of plastic foams have been successfully used for packaging. It has been claimed *that expanded polyethylene is the best cushioning material. Polystyrene and poly-

*Calvin J. Benning, Plastic Foams, Vol 11, Wiley-Inter-science, 1969.

urethane foams are used widely as packaging materials. However, none of these plastic foams are biodegradable or water-soluble. Their disposal after use thus can cause environmental problems unless they are collected and specially treated.

A foam consists of a mass of gas bubbles dispersed in a solid or liquid matrix. For this study, the liquid matrix was an aqueous solution of a high concentration of water-soluble polymer (e.g. gelatin). The gas bubbles were supplied by use of air, vaporized water, compressed nitrogen, a chlorofluorocarbon, heated ammonium carbonate $[(\text{NH}_4)_2\text{CO}_3]$, and nitrogen-generating organic blowing agents. A surfactant was used to reduce the surface tension of the solution so that it could be more easily expanded.

The sol/gel transition for gelatin occurs between 30 and 40°C thus providing a convenient method for stabilizing the foam. Solutions of other water-soluble polymers do not gel on cooling to normal temperatures. Therefore, when polyvinyl alcohol solution, for example, was foamed, it was necessary to add a crosslinking agent (resorcinol) to gel (stabilize) the foam.

The addition of resorcinal to polyvinyl alcohol solution results in the formation of thermally reversible gels. The gel rate depends on the polymer concentration, the amount of resorcinol added, and the temperature of the mixture. The polyvinyl alcohol foam produced in this program gelled overnight at room temperature (20-25°C). The polyvinyl alcohol foams are superior to gelatin foams in recovery after compression, and are less expensive.

2.2 MATERIALS AND EQUIPMENT

Tables 2 and 3 list, respectively, the materials and the equipment used in this program.

Tradenames in this report are used for convenience to designate some of the materials and equipment. Citation of such names does not constitute an official endorsement or approval of their use. The generic name for each such item is given in Tables 2 and 3.

2.3 GELATIN FOAM DEVELOPMENT

Gelatin was selected as the pioneer model material for this program. Successful foaming processes for gelatin would serve as the basis for the development and evaluation of similar systems for other water-soluble polymers.

Gelatin is a derived protein made from the refined extract of collagen (animal connective tissue). It forms clear, viscous solutions in water. The gelatin molecule is made up of amino acids joined together by amide linkages in a long molecular chain. There are 18 different amino acids in gelatin.

Gelatin is extracted from animal tissues which contain high proportions of collagen. The tissues are pretreated (cured) with acid or lime. "Type A" gelatin is derived from acid-cured tissue. "Type B" gelatin is derived from lime-cured tissue.

TABLE 1
METRIC CONVERSIONS

<u>Quantity</u>	<u>English Unit</u>	<u>SI Unit</u>	<u>To Convert English Unit to SI Unit Multiply By:</u>	
Length	inch	meter	2.540000	E-02
	foot	meter	3.048000	E-01
Volume	cubic foot	cubic meter	2.831685	E-02
Density	lb/cu ft	kg/cu meter	1.601846	E+01
Pressure	p.s.i.	pascal	6.894757	E+03
Viscosity	cp	pascal-second	1.000000	E-03
Temperature	°F	°C	$t_c^{\circ} = (t_f^{\circ} - 32)/1.8$	
Heat Energy	btu	joule	1.054350	E+03
Price	\$/lb	\$/kg	2.204622	E-00

Table 2

MATERIALS USED

<u>Type or Function of Material</u>	<u>Trade Name or Type</u>	<u>Manufacturer</u>
<u>Polymers</u>		
Gelatin	610 Colloid (6/20 mesh)	Swift and Company
Gelatin	Type 14X (8 mesh)	Wilson and Company
Polyvinyl alcohol	Gelvitol 1-30 brand	Monsanto Company
Ethylene/maleic anhydride copolymer	EMA-54 brand	Monsanto Company
Polyvinyl pyrrolidone	PVP K-15 & K-30 brands	GAF Corporation
Acrylonitrile/methyl vinyl pyridine copolymer	AP-250 brand	Monsanto Company
Urea/formaldehyde	RAPCO Foaming Resin RAPCO Foaming Agent	The Adams-Barre Company (Columbus, Ohio)
<u>Foaming Agent</u>		
Ethylene oxide adduct of lauryl sulfate (30% solution)	H1-Ex Type 15 AE & 35 brand	W. H. Kilde and Company

Table 2 (cont'd)

Type or Function of Material	Trade Name or Type	Manufacturer
<u>Blowing Agents</u>		
Ammonium carbonate	Keystone brand	Agrico Chemical Company West Germany
Azobisisobutyronitrile	VAZO brand	Du Pont Company
Compressed nitrogen	prepurified	Air Reduction Company
Trichlorofluoromethane	Ucon 11 brand	Union Carbide Corporation
Dichlorodifluoromethane	Ucon 12 brand	Union Carbide Corporation
<u>Nucleating Agents</u>		
Aluminum silicate		Phillips Petroleum Company
Carbon black	Monarch 1100 brand	Cabot Corporation
Glass microballoons	Eccospheres ID101 brand	Emerson and Cuming Inc.
<u>Gelatin Crosslinking Agents</u>		
Formaldehyde	30% aqueous solution with 10-15% methanol as a preservative	MC/B Manufacturing Chemists
Glutaraldehyde	50% aqueous solution	Union Carbide Corporation

Table 2 (cont'd)

<u>Type or Function of Material</u>	<u>Trade Name or Type</u>	<u>Manufacturer</u>
<u>Polyvinyl Alcohol Crosslinking Agent</u>		
Resorcinol	--	Koppers Company
<u>Polyvinyl Pyrrolidone Crosslinking Agent</u>		
Sodium Hydroxide (NaOH)	ACS Grade	MC/B Manufacturing Chemists
<u>Foam Humectants</u>		
Ethylene Glycol	---	Ashland Chemical Company
Glycerine	99% grade	Colgate-Palmolive Company
Mineral Oil	Paraffin oil (light)	MC/B Manufacturing Chemists
<u>Gelatin Preservative</u>		
Sodium pentachloro- phenate (NaPCP) C_5Cl_5ONa	Santobrite brand	Monsanto Company

Table 3

EQUIPMENT USED

<u>Name</u>	<u>Manufacturer</u>	<u>Used For</u>
MRC Lab Foam Generator	Developed by Monsanto Research Corporation	making water-base, high expansion foam from low concentration polymer solution and Hi-Ex foamer
UFC Foam Generator	The UFC Corporation	generating urea/formaldehyde foams in commercial applica- tions
Oakes Mixer (model 4BMIA)	The E. T. Oakes Corporation	generating various types of foams
Z-Blade Micro-Mixer (model 4-LP)	The Atlantic Research Corporation	homogenizing high concen- tration gelatin/water mixtures
Waring Blendor (model 5011)	The Dynamics Corpor- ation of America Waring Products Div.	mixing, homogenizing and air frothing
Plastic Extruder (3/4 inch)	C. W. Brabender Instruments, Inc.	extruding polymers
Plunger Injection Molding Machine (V-1-5)	The Farrel Birming- ham Company, Watson- Stillman Press Div.	molding polymers
Microwave Heater (Model EW3-DPM3S)	Varian Industrial Microwave Systems	rapid curing and drying
Vacuum Oven	Lab-Line Instruments	low temperature drying
Melting Point Apparatus Fisher-Johns	The Fisher Scien- tific Company	melting point

"Type A" gelatin is more abundant and was used exclusively for this study. High molecular weight gelatins (Wilson 14X or Swift Type 610) were selected because, as high molecular weight materials, they form gels readily and the dried polymer films and castings have higher strengths than those made from low molecular weight materials.

Gelatin is sold in a dry, granular form. The specific gravity of dry gelatin is approximately 1.25. However, its bulk density is about 0.65 g/cc (40 lb/cu ft). The average weight of gelatin in a 55-gallon fiber drum is about 325 pounds.

2.3.1 Preparation of Gelatin Solutions

Granular rather than powdered gelatin is preferred in making high concentration (20-40% gelatin) solution. The powdered form has a tendency to cake during the process of dissolving. Normally, gelatin is stirred into hot water (80-90°C) heated on a water bath. Stirring is continued until a homogenous solution is obtained. An Atlantic Research Z-blade Micro-Mixer was used to prepare solutions with very high gelatin contents (75% gelatin).

One part sodium pentachlorophenate (NaPCP) was used for every 1000 parts of gelatin to preserve the gelatin from putrefaction in solution.

Gelatin/glycerine/water solutions were prepared by adding gelatin to the glycerine/water mixture and heating as above on a water bath.

2.3.2 Evaluation of Foaming Processes

2.3.2.1 Approaches to Foam Formation

Three general approaches to producing an environmentally degradable foam packaging material were investigated. These three approaches are presented in their broad sense in Figure 1.

2.3.2.2 Perspective on Pour-in-Place Foam Production

The principal difficulty in producing a pour-in-place environmentally degradable foam packaging material centered on the problem of removing or circumventing the effects of large amounts of water in the foam. Water was necessarily present because gelatin and most other environmentally degradable polymers are water soluble. Water must also be present in large amounts (ranging from 90-50% of the formulation) to give solutions of processable viscosities. Table 3 gives the viscosities of several water-soluble polymers over a range of compositions.

In order to make a pour-in-place foam that develops high early strength, a number of alternatives were investigated. They were:

- (1) Reduce the water content to the point at which the polymer/water mixture has good strength at normal temperatures, but can be made to flow under pressure at elevated temperature and can be made to foam when heated to a suitable temperature.

ENVIRONMENTALLY DEGRADABLE FOAM PRODUCTION

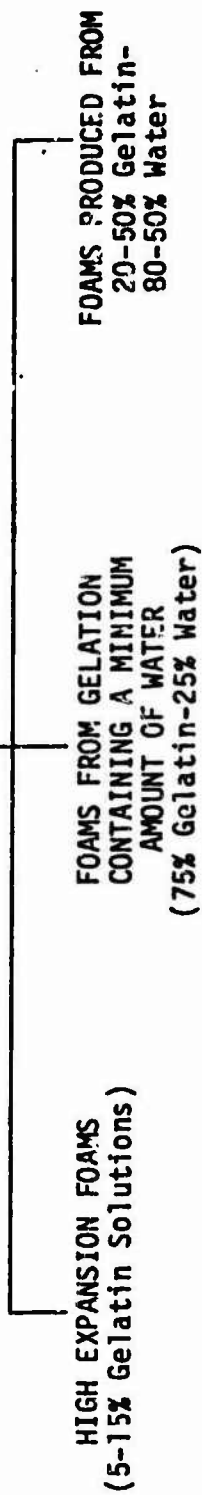


Figure 1. General Approaches to Producing an Environmentally Degradable Foam

Table 4

VISCOSITY (Cp) OF AQUEOUS SOLUTIONS
OF THREE WATER-SOLUBLE POLYMERS

Solution Concentration (% Polymer)	Polymer		
	Gelatin Swift 610*	Polyvinyl Alcohol Gelvaton 1-30**	Ethylene/Maleic Anhydride EMA-54***
1	2	1	100
3	-	-	800
5	3	5	3,000
7	6	-	8,500
10	14	12	-
20	84	1,000	-
30	-	10,500	-
40	-	-	-
50	1,775	-	-

* Viscosity determined at 55°C. Solutions of concentrations over 5% will gel at room temperature.

** Viscosity determined at 20°C.

*** Viscosity determined at 25°C.

Note: The viscosities of polyvinylalcohol and ethylene maleic anhydride solution at 55°C were not determined.

- (2) Produce foam products that, because of their geometry, lose water readily and thus develop strength.
- (3) Produce foams or froths that, because of the extreme smallness of the bubbles, have some degree of strength, permitting pouring in place around the objects to be packaged.

These approaches are described in detail in the following sections.

2.3.3 Water-Base High Expansion Foams

High expansion foams were initially developed in England for use in fighting coal mine fires. To generate such a foam, an aqueous solution of a foaming agent (98.5% water, 1-1/2% foaming agent) is sprayed onto a cloth screen. A stream of air is blown through the screen and a mass of bubbles forms on the downstream side of the screen. With water/foaming agent solutions, expansion factors (volume of foam/volume of solution) of 1000/1 are obtained.

Figure 2 presents a schematic diagram of a high expansion foam generator system. Large-scale foam generators of this type are currently used as truck-mounted units by fire departments.

In previous work done at Monsanto Research Corporation, such foam generation systems were modified to spray polymer solutions to produce foams the strength of which was increased by a dissolved polymer. Gelatin was used in most of these systems. The gelatin-containing foams had expansion factors ranging from 50/1 to 600/1. These foams dried to produce masses of foam which were

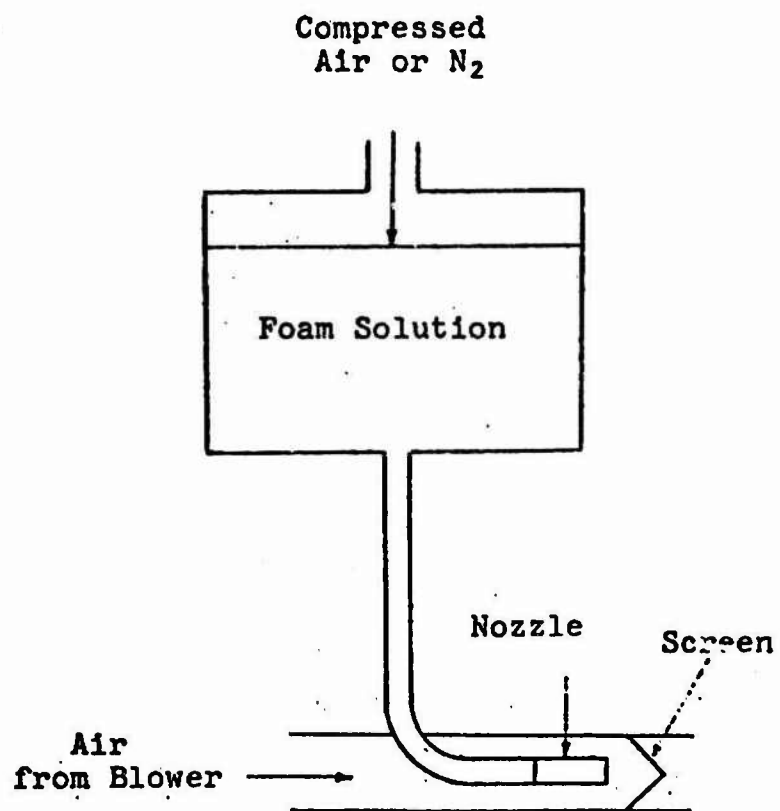


Figure 2. Schematic Drawing of the Foam Generator

stable. Compression of these foams gave masses of interconnected fibrous materials suggestive of a non-woven fabric.

The first foams made were of the high expansion foam type. Solutions containing 15% gelatin were sprayed and blown into foams. These foams were collected in boxes and dried. Drying took several days, and the foams produced could be collapsed into mats that could be used as an environmentally degradable stuffer for packaging.

However, this process did not appear to be suitable to produce a pour-in-place foam for encapsulating an item to be packaged. The foams were too weak as poured to support the weight of an encapsulated item, and the long drying time would make this pour-in-place use unattractive.

Moreover, the contracting agency indicated a strong interest in a pour-in-place foam and had little or no interest in a stuffer-type packing. For these reasons, the development of high expansion foams was abandoned after the first month of the program.

2.3.4 Foams from Gelatin Containing a Minimum Amount of Water

This approach to producing foams involves the use of gelatin (or other water-soluble polymers) as the major component, and water, either alone or with plasticizers, as the minor component.

The water content was held to 25% of the total weight of the mixture. Because of the large amount of polymer used, a great deal of mechanical work had to be done to obtain a homogeneous mixture. The extremely viscous doughs could then be made to foam by applying heat to vaporize the water in them, or by the use of both heat and vacuum. The methods used in this approach are presented schematically in Figure 3.

The thrust of this work was to produce a tough, doughy material that could be foamed directly by forcing it through a heated die attached to either an extruder or an injection molding machine. An alternative approach was to extrude the dough at low temperatures ($\sim 40-50^{\circ}\text{C}$) to form a strand that could be subsequently foamed.

It was our purpose by either means to produce a foamed material that could be cut into small "pillows" which could be poured around an article to be packaged. If a coherent mass of foam were necessary, the individual pillows could be made to adhere to each other by lightly misting them with water or dilute polymer solution, as they are poured.

2.3.4.1 Use of Laboratory-Scale "Z" Blade Mixer

As a preliminary step to producing foams, the use of a laboratory scale "Z" blade mixer (in effect a miniature Banbury mill) was used to mix homogeneous mixtures of gelatin (75% by wt) and water

ENVIRONMENTALLY DEGRADABLE FOAMS
PRODUCED USING A MINIMUM OF WATER
(75% WATER SOLUBLE POLYMER)

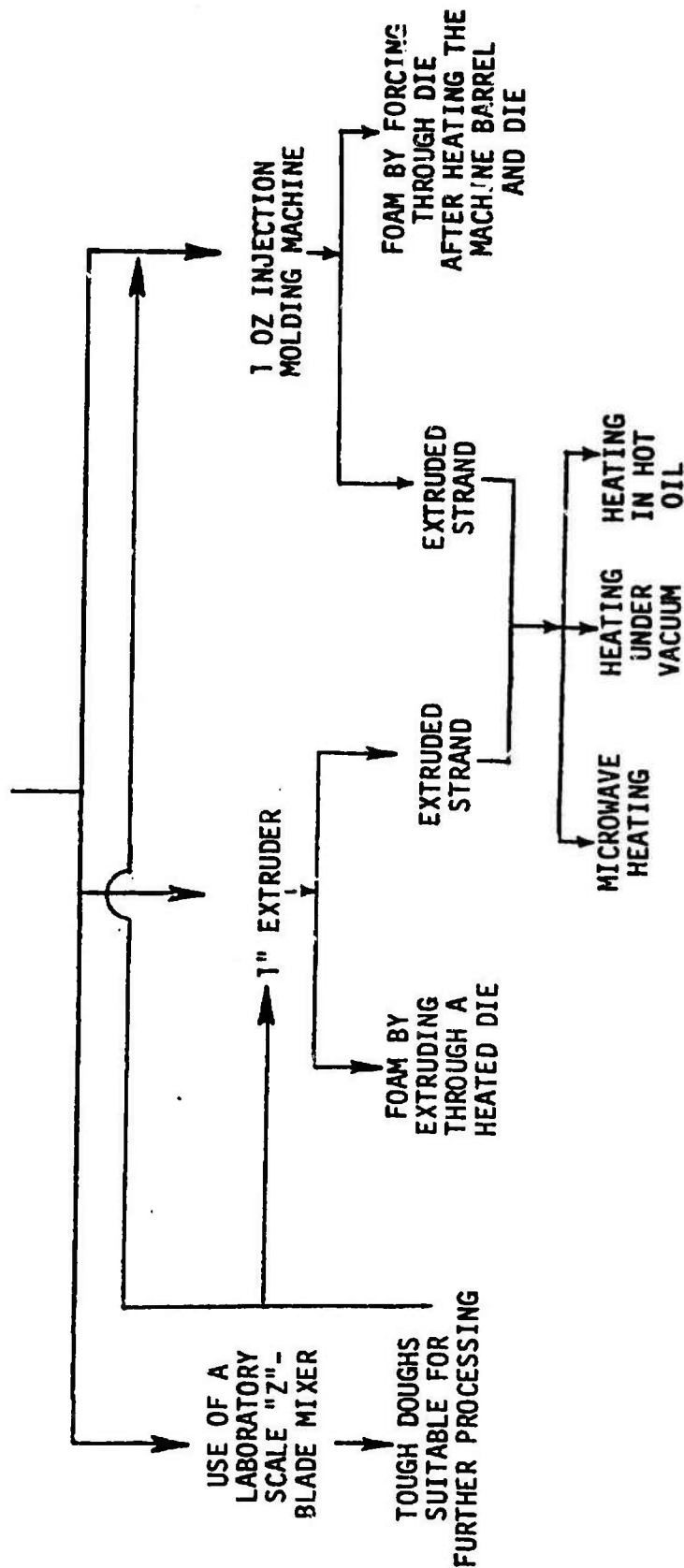


Figure 3. Preparation of Foams From Highly Concentrated Polymer (Gelatin) Solution

(25% by wt). Mixing in this equipment was done at room temperature. The only increase in temperature was due to the mechanical work done on the material by the high shear mixer. With this equipment, tough doughs could be produced that were suitable for processing in an extruder or in an injection molding machine.

The preparations had small amounts of nucleating agents or pneumatogens added to them if needed while they were in the mixer.

2.3.4.2 Use of One-Inch Extruder

Our first approach to producing a pour-in-place type foam involved the use of a one-inch extruder fitted with a strand die. Figure 4 is a schematic drawing of the extruder.

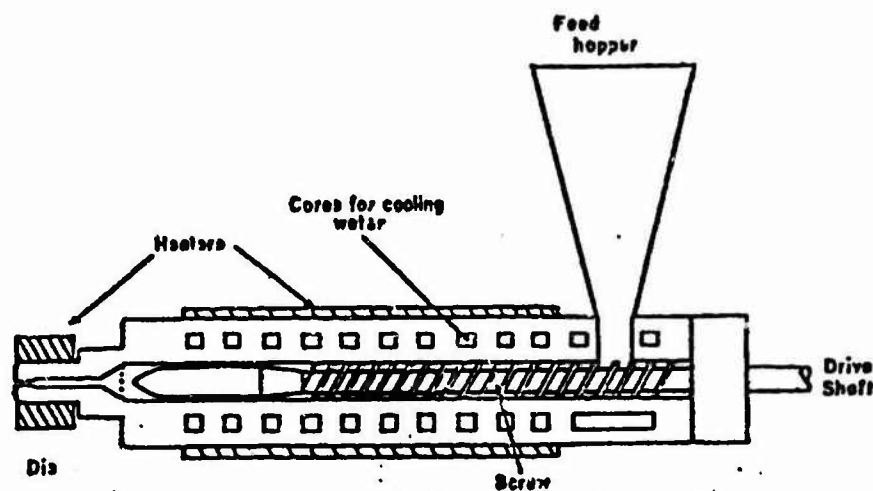


Figure 4. Diagram of Plastic Extruder

Gelatin plus water (75:25 parts by wt) from the "Z" blade mixer experiments was fed to the extruder. Alternatively, a mixture of granular gelatin plus the necessary amount of water was fed to the machine and homogenization took place in the extruder barrel.

It was found during this work that the strand did expand as it left the die. The foam produced had an irregular bubble structure and the foam collapsed on cooling. The melted gelatin was very adhesive. If the material as it left the die contacted the die face, it adhered there and a strand was not produced. Under these conditions, a pear-shaped mass of foam was produced which continued to grow as long as the extruder was running. These masses of foam collapsed on cooling.

Considerable difficulty was also experienced with the highly viscous, adhesive gelatin melt binding the extruder screw in the extruder barrel. This happened if the extruder had to be shut down momentarily, or if the temperature of the extruder barrel or die was lowered. Once this happened the entire extruder had to be dismantled and cleaned.

Because of the inferior product produced and the difficulties encountered in keeping the extruder running, this approach was abandoned.

However, a quantity of unexpanded strand was produced by running the extruder at 90°C. This strand was subsequently foamed using the techniques described in Section 2.3.4.4.

2.3.4.3 Use of One-Ounce Injection Molding Machine

An alternate approach to forming a foamable high gelatin material was to pass the product from the "Z" blade mixer (Section 2.3.4.1) through a one-ounce injection molding machine.

This machine, which is shown schematically in Figure 5, is much simpler than an extruder, and hence easier to maintain and clear. It consists of a plunger which is pushed into a barrel. Force is supplied by a hydraulic ram. The barrel of the machine is pre-loaded with the material that is to be molded. The ram fits closely to the inside diameter of the barrel. As force is applied, the polymer is extruded through the nozzle, and ordinarily is injected into a mold.

For this work, the mold was removed and the strand was extruded into the air. In early experiments the barrel was heated to from 100 to 120°C. A foam strand was produced which collapsed on cooling. Difficulty was experienced with the ram seizing in the barrel. This was particularly true when the initial charge of gelatin plus water had been forced from the barrel and the plunger or ram was withdrawn. A sufficient film of gelatin remained on the barrel wall to make removal extremely difficult.

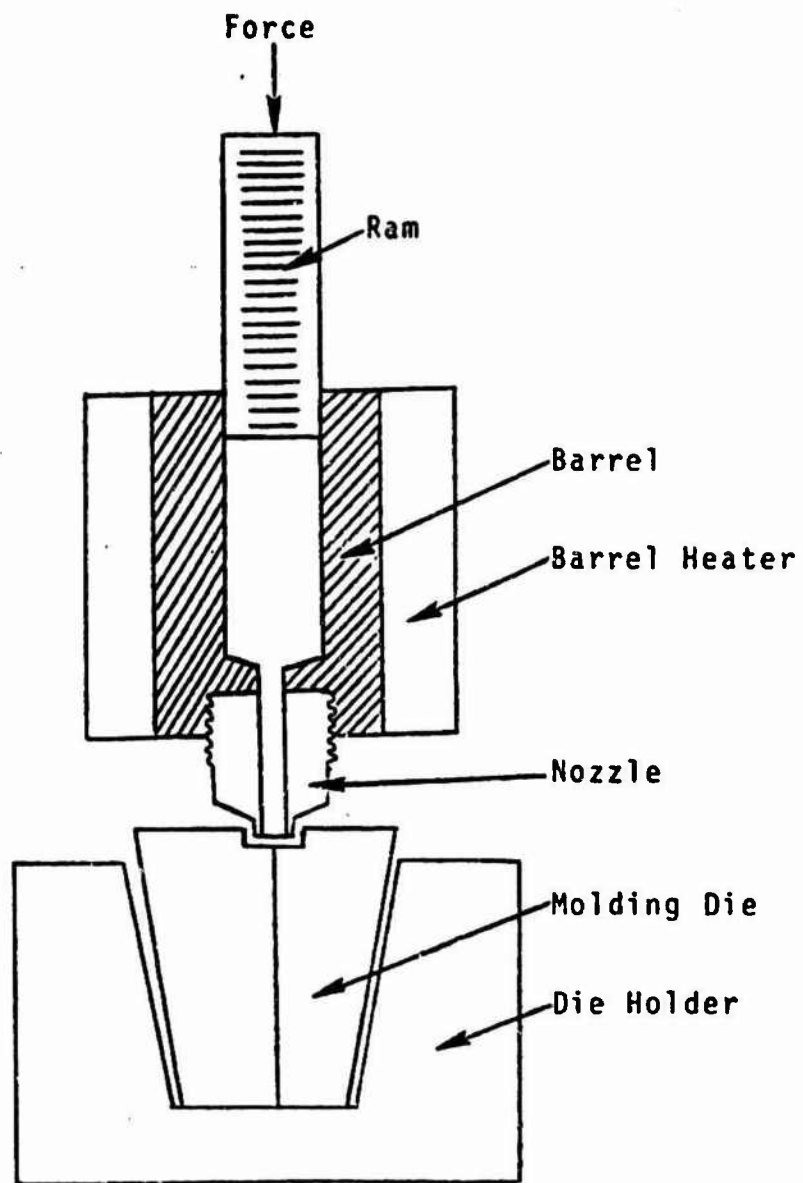


Figure 5. Schematic of Injection Molding Machine

Better success was achieved with the 75% gelatin material when the temperature was kept at 90°C. No foaming resulted but a strand suitable for further work was obtained.

The best results were obtained when a gelatin/water dough with 66% gelatin was mixed in the "Z" blade mixer and then extruded at 40°C. Good quality rubbery strands were produced, and no difficulty was experienced with the ram seizing in the barrel.

All strands used in subsequent heating and foaming experiments were produced by this method.

2.3.4.4 Foaming of Strand by Use of Heat

The dough-like materials produced by the "Z" blade mixer and the unfoamed strands produced by the extruder and injection molding machine were heated in several different ways to determine if high quality foams could be produced.

The gelatin/water mixtures were heated using microwave energy. A Varian microwave generator and conveyORIZED oven was used for this work. It was believed that the water would be uniformly heated by the microwaves and the entire mass of gelatin would foam when the water was converted to steam. A range of power settings from 0.5 to 2.5 kW and various dwell times in the oven were used. In all cases,

the gelatin/water dough foamed very well while it was in the oven, but on removal from the heating zone the foam collapsed on cooling. Investigation of the collapsed foam indicated the steam bubbles had coalesced into a single larger bubble. On cooling, the steam condensed producing a partial vacuum in the bubble.

A second approach to producing foams of the gelatin/water doughs and strands was to heat them in a vacuum oven. Thirty inches of vacuum was used in all cases. A range of temperatures from 70 to 110°C was used for this work. At all temperatures the results were similar to those experienced using microwave energy. The samples foamed vigorously as the temperature was raised from 70 to 110°C. However, in all cases, the foams collapsed when the oven was brought to atmospheric pressure.

The best results in foaming the gelatin/water strands were achieved by dropping pieces of the material into heated mineral oil. This was a process similar to deep fat frying. A range of oil temperatures from 100 to 140°C was used. Both 75% and 66% gelatin preparations were used. It was found that at the lower concentration and at temperatures less than 125°C the gelatin dough melted on the surface of the oil and then sank to the bottom of the vessel. When this

occurred, no foam resulted. However, at the higher concentration and at temperatures greater than 125°C, the gelatin floated on the surface and the water vaporized to produce a foam. The best results were obtained when the oil temperature was 140°C. Under these conditions, pieces of gelatin foam resulted. These foams were somewhat coarse-celled and they were dimensionally stable.

The general approach of foaming high gelatin content materials was abandoned at this point because the doughs were difficult to process, and the products produced were not of good quality.

2.3.5 Use of 20-50% Polymer Solutions

It appeared that concurrent studies on gelatin solutions in the 20-50% gelatin content range offered a better chance of producing a usable foam material for packaging applications.

This general approach offered the best means of achieving a pour-in-place environmentally degradable packaging material. The various methods of producing such foams using 20-50% gelatin solutions are presented schematically in Figure 6.

2.3.5.1 Use of An Oakes Mixer

MRC had previously developed a frothed epoxy foam for packaging application using an Oakes Mixer. Figure 7 is a schematic diagram of this machine. Figure 8 is a photograph of the machine used in this work. The mixing head of the mixer consists of a metal

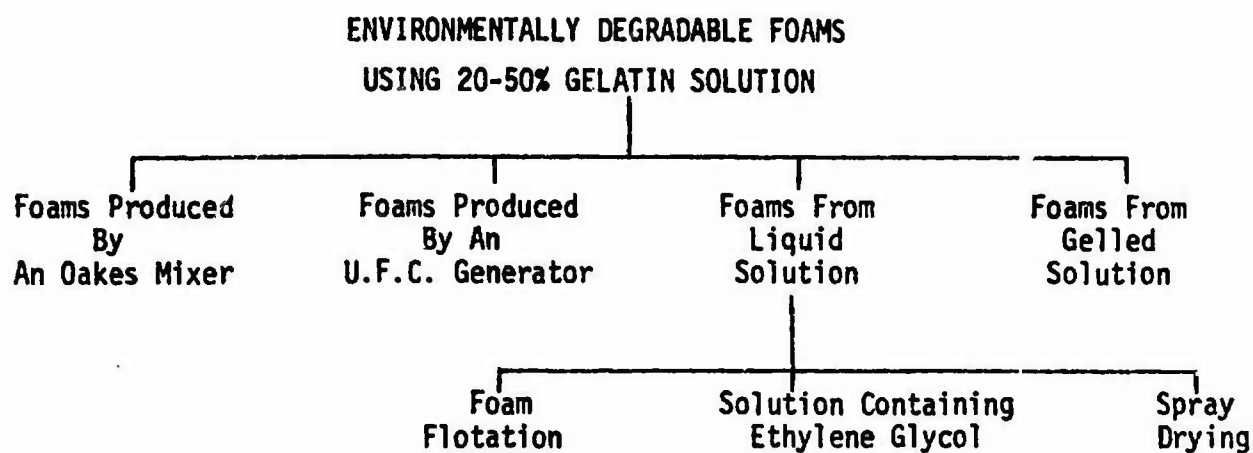


Figure 6. Production of Foam from Low and Intermediate Concentration Polymer (Gelatin) Solutions

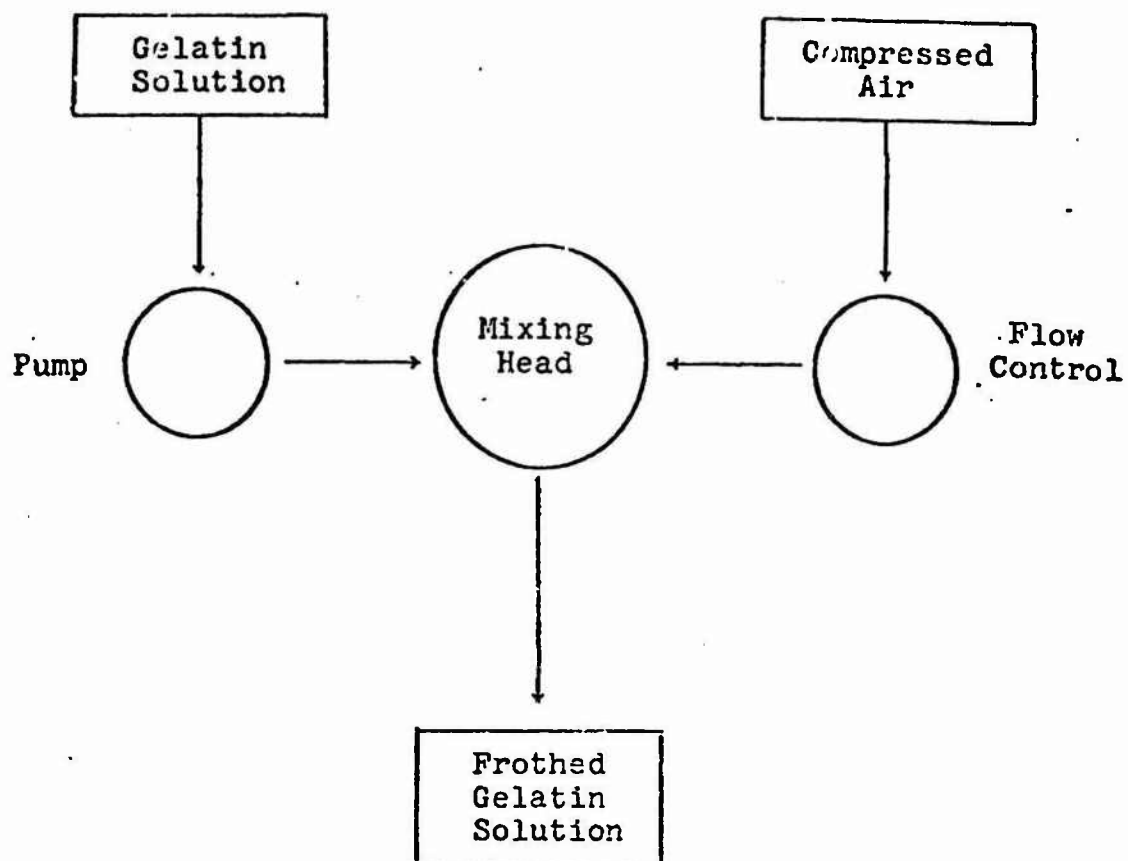


Figure 7. Schematic of Oakes Mixer

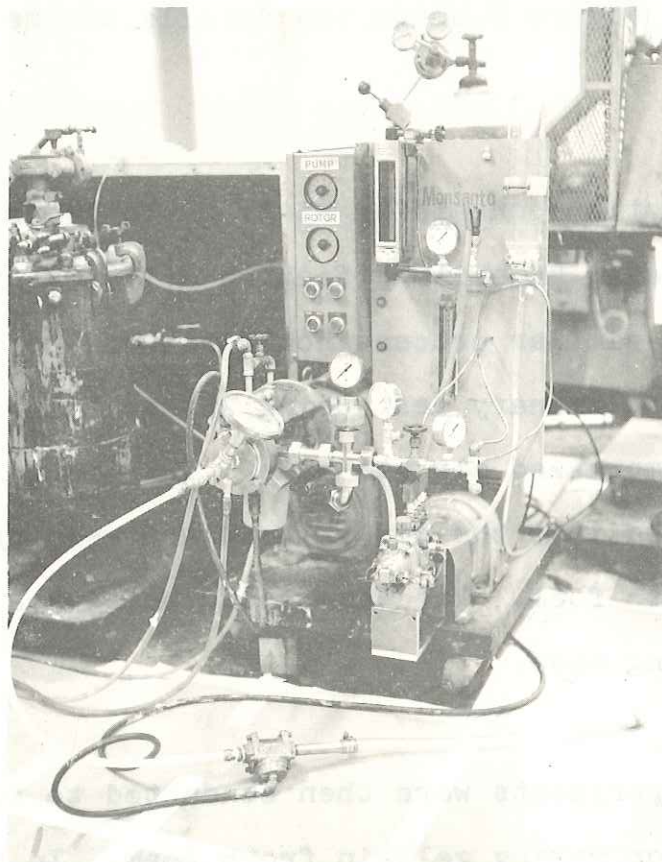


Figure 8. Oakes Mixer and Associated Equipment

disc which rotates. Both the disc and the inside surfaces of the end pieces of the head are serrated with concentric rows of teeth. The teeth of the disc fit between the teeth on the mixer's end pieces. During operation, the disc rotates against the end pieces. Thus, when a liquid and a gas are fed into the mixing head, the mixture is squeezed between the teeth under high shear and becomes homogenously mixed. Normally, a froth can be produced by this process. Figure 9 shows the details of the interior of the Oakes mixer.

Since gelatin solution containing H1-Ex could be frothed by air in the U.F.C. Foaming Generator (Section 2.3.5.2) it seemed reasonable that a similar process could be carried out using the Oakes Mixer. A preliminary test using 25% gelatin solution plus 1.5% H1-Ex and compressed air was made. The liquid and gaseous components were fed into the mixing head and were processed into a very stable froth foam. The foam could be set as quickly as 3 hours after being made.

Nine series of experiments were then conducted to further evaluate the Oakes Mixer for making gelatin froth foam. In the first series of tests, 50% gelatin solution was frothed with air. The gelatin solution was highly viscous and clogged the mixing head after six samples had been taken.

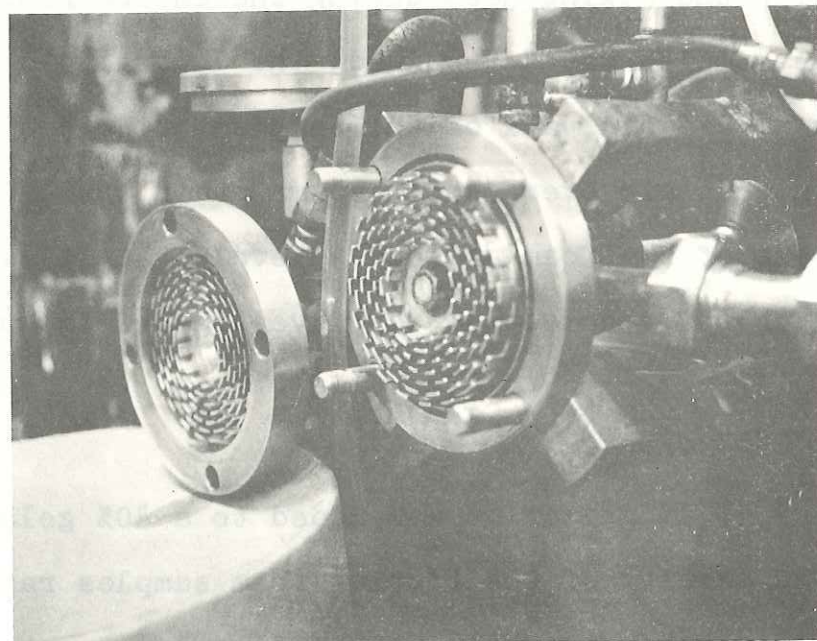
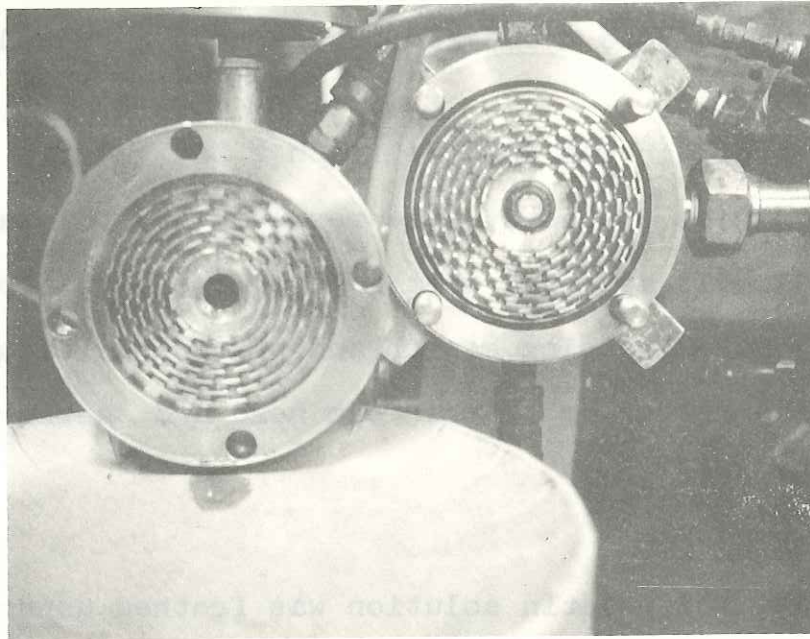


Figure 9. Interior of Oakes Mixer Head

The density of the samples ranged from 25 to 30 lb/cu ft. These samples remained flexible when kept under 100% relative humidity conditions. However, if left in the open air for 3 hours or longer, the foam samples dried and became very hard and inflexible.

A larger amount of air was used to froth a 50% gelatin solution in the second series of tests. The results were the same as those of Series No. 1. It appeared that a lower concentration gelatin solution would make frothing easier and prevent difficulties with the foam machine (clogging of the foam head and seizing of the shaft of the mixer).

In series No. 3, 40% gelatin solution was frothed using the same air flow as in series No. 2. No difficulties were experienced with the mixing head during the entire run. The density of the samples was determined; the lowest value was 11.6 lb/cu ft. Again, all of the samples dried out when placed in open air overnight. To maintain the moisture content of the foam at such a level that it remains flexible, the use of a humectant was investigated in subsequent runs.

In series No. 4, 1.2% glycerine was added to a 40% gelatin solution. The density of the frothed foam samples ranged from 15.5 to 21.8 lb/cu ft. All the samples dried out when placed in open air overnight.

In series No. 5, 40% gelatin solution containing 3% glycerine was frothed with Ucon 11 (a fluorocarbon) instead of air. Homogeneous cell size and high expansion foam was obtained. However, the foam collapsed badly on standing. The collapse was due to the condensation of the Ucon 11 (b.p. 23.8°C) as the foam cooled to room temperature. The condensation created a partial vacuum inside the foam bubbles. The density of the sample two hours after foaming was 11.4 lb/cu ft. Again, all the samples dried out when placed in open air overnight.

Series No. 6, 7, 8 and 9 were conducted with 40% gelatin solution, using Ucon 12 (b.p. -29.8°C) as the pneumatogen. Solutions frothed in series No. 6, 7 and 8 contained 10%, 15% and 20% glycerine, respectively. Froth foam blocks (12 x 12 x 18 in.) and rods were prepared. The rods (5/8 to 3/4 inch diameter) were cut into 1-inch long "pillows". The highest block density was 6 lb/cu ft. The bulk density of the "pillows" ranged from 2 to 3 pounds/cu ft. The 40% gelatin solution containing 20% glycerine produced a froth foam with much better moisture retention; it was therefore softer and more resilient.

In series No. 9, measurements were made to obtain quantitative data on froth production. A solution of 40% gelatin and 20% glycerine was frothed in the Oakes Mixer. The solution viscosity was 660-930 cp at 65°C. During the frothing process,

3.6 grams of Ucon 12 was used for every 100 grams of 40% gelatin/20% glycerine solution. The froth process was run at 38-44°C. This is just above the gelation temperature for the gelatin solution. The foam density was 5.7 lb/cu ft.

Following the series of tests described in the preceding paragraphs, froth gelatin foam samples were prepared with the objective of making 10 cu ft of foam blocks and 10 cu ft of foam "pillows". During the sample preparation, different foaming conditions and solutions of various concentrations were further evaluated. By this means, additional quantitative process data were obtained. During this work, a foam frothing process based on Hi-Ex/nitrogen was preliminarily optimized.

The first samples prepared during this portion of the program were made using a solution containing 40% gelatin and 20% glycerine. This solution tended to clog the mixing head of the Oakes Mixer on long runs. Therefore, 30%, 20%, and 10% gelatin solutions (containing 15%, 10%, and 5% glycerine, respectively) were processed. Foam block samples, made by frothing these solutions with Ucon 12, had very irregular cell size. Thus, this foaming process appeared not suitable for making large samples unless improved by further study. Most of the foam block and foam "pillow" samples were prepared by frothing gelatin solution containing Hi-Ex with nitrogen. The following procedures were used:

Hi-Ex foaming agent (1.5% by wt) was added to the gelatin/glycerine solution and the mixture was heated in an oven (to 90°C for 30% solution; to 70°C for 20% or 10% solution). The heated solution was poured into the feed tank of the foam generator and recirculation was started through the mixing head. This served to heat the mixing head to about 40°C. Frothing with nitrogen was begun at the same time. When the temperature of the solution had decreased to 35-45°C, and the foam mixing head temperature was 37-45°C, discharge of the froth foam was started into cardboard boxes (for making blocks) or spread into ribbons upon a piece of kraft paper. These ribbons were then cut into small "pillows".

The following samples were prepared for delivery to the US Army Natick Research and Development Command.

(1) Hi-Ex/Nitrogen frothed:

- . Foam blocks and "pillows" from 30%/gelatin/15% glycerine solution.
- . Foam blocks from 20% polyvinyl alcohol (Gelvatol 130)/20% glycerine solution crosslinked with resorcinol.
- . Foam "pillows" from 10% gelatin/5% glycerine solution.

(2) Ucon 12 frothed:

Foam blocks from 30% gelatin/15% glycerine solution.

Overall, about 10 cu ft of foam block samples and 10 cu ft of foam "pillow" samples were submitted to US Army Natick Research and Development Command.

These sample preparation methods served to demonstrate the feasibility of making low-density gelatin foam blocks or "pillows". Engineering work would have to be done to develop a compact and portable foam generator and to optimize the foam process.

The mixer and its attendant tanks and fittings could be easily rendered portable by rearranging the present equipment and mounting on a pallet or cart. Utilities which would be needed are a compressed nitrogen or air supply, and electrical service to heat the polymer solution and water for cleanup and to drive the mixing head. As mentioned before, a fully optimized practical process must be developed for making foam-in-place or pillow-shaped gelatin or other polymer foam for packaging applications. It would be appropriate to develop the process first and then align the equipment according to the finalized process. For example, to make foam "pillows" in quantity, foam rods could be generated from multiple nozzles in parallel. Carried by a receiving belt, the rods might run through a cooling chamber and thus be "set" promptly. After this, they would go through a cutter to form the desired "pillows".

The gelatin rods could be set in 10 seconds when placed in a cold chamber. Blocks would require a longer time because of the poor heat transfer through the larger mass of foam. The actual time to set these foam blocks when chilled was not determined during this study.

a. Cost Estimates

The Oakes Mixer appears to be an adequate piece of equipment for making gelatin or other water-soluble polymer foam. Gelatin foam blocks or foam "pillows" prepared by frothing gelatin/glycerine solution with Hi-Ex/nitrogen contain gelatin, glycerine, Hi-Ex, water and a very small amount of sodium pentachlorophenate. The lowest density foam blocks made during this program had a density of 1.24 lb/cu ft. The lowest bulk density of the foam "pillows" was 0.77 lb/cu ft. In this study, food-grade gelatin was processed. It costs \$2.75/lb. Glycerine costs about \$1.50/lb. Assuming two parts of gelatin and one part of glycerine to be the main ingredients of these foamed products, gelatin foams would cost \$2.33 per pound. This cost is for materials only. If these foams were made in quantity, a total price of about \$2.50 per pound is predicted.

These costs could be reduced by using a lower grade gelatin or other less expensive water-soluble polymer. Purchasing in large quantities would also help to reduce the price. Hi-Ex

is a proprietary product and as such is sold at a premium price. It could be replaced by other surfactants that are sold as chemical commodities. Examples of such materials are Neodol (Shell Chemical Company), Retzanol (Retzloff Chemical Company), Aviral (Henkel Company) and Tergitol (Union Carbide). We have had experience with Tergitol in another program and it produces good quality foams.

Other water-soluble polymers that might be used are less expensive. Polyvinyl alcohol costs about \$1.00/lb. Ethylene/maleic anhydride copolymer costs \$1.50/lb while polyvinylpyrrolidone costs about \$2.00/lb.

Only polyvinyl alcohol was processed into foam during this program. The material cost for polyvinyl alcohol foam is estimated to be approximately \$0.94/lb. Residual water and resorcinol reduces the price below the \$1.00/lb anticipated. Total cost, including labor and utilities, is predicted to be about \$1.10/lb.

b. Gelatin Foam Properties

Gelatin foam samples prepared from 40% gelatin/20% glycerine solution were tested with the following results;

a. Compression Strength (by ASTM D1621)

At 10% Compression 11 psi

At 60% compression 24 psi

b. Tensile Strength (by ASTM D2406)

Ultimate tensile strength 9.8 psi

Ultimate elongation 164%

c. Moisture Absorption (by ASTM 2842-69)

After 2 hours 250%

After 24 hours Mostly disintegrated

d. Flammability (by ASTM D1692-68)

Burning extent 2.5 in.

Burning rate 1.85 in./min.

SE (self-extinguishing) 2.5 in. burned in 82 sec.

e. Thermoconductivity (by ASTM D2236-70)

0.20 Btu·in./ft²·hr·°F

f. Water Vapor Transmission (by ASTM C355-64)

WVT (Water Vapor Transmission) 350 g/24 hr·m²

Permeance 0.332 metric perms

Permeability 0.652 metric perm-cm

2.3.5.2 Use of a UFC Mixer

The UFC foam generator (Figures 10 and 11) has been developed for generating urea/formaldehyde foams in commercial applications. It permits the introduction of air or nitrogen into a liquid stream containing water, foaming agents, and a catalyst. The gaseous phase and liquid phase are intimately mixed in a chamber filled with glass beads. A second liquid line permits introduction of the urea/formaldehyde prepolymer into the already mixed gas and liquid stream. As the mixture comes out of the generator, the pressure is released and the gas-saturated liquid froths and produces a fine celled foam.

Work on the production of foams using the UFC generator preceded and was concurrent with the work with the Oakes Mixer. Four general types of foam were investigated. They were:

Gelatin froth foams

Urea/formaldehyde foams

Urea/formaldehyde foams containing gelatin

Urea/formaldehyde foams containing polyvinyl alcohol

a. Gelatin Froth Foams

The initial attempt to make a gelatin froth foam was made on the UFC generator as supplied by the U.F. Foam Company. Production of foam using a 40% gelatin solution heated to

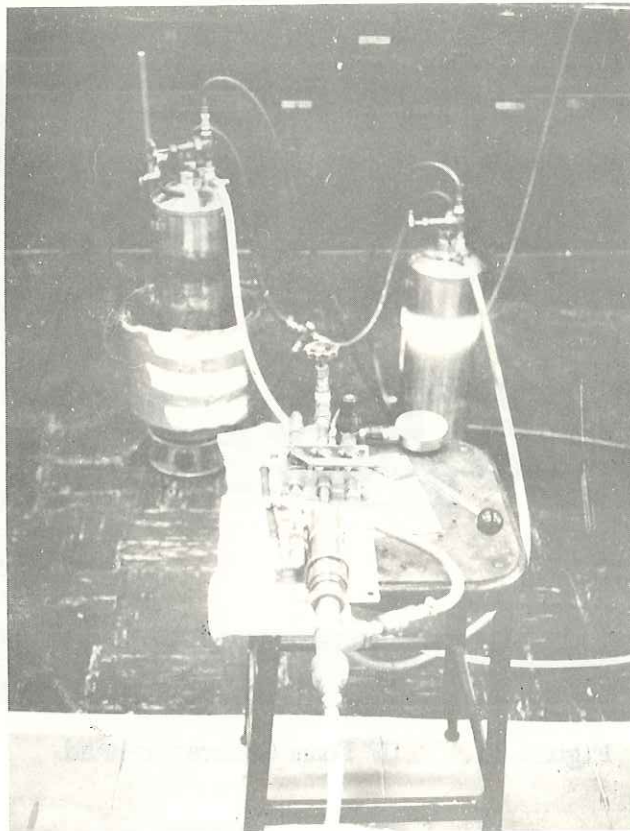


Figure 10. Overall View of UFC Foam Generator

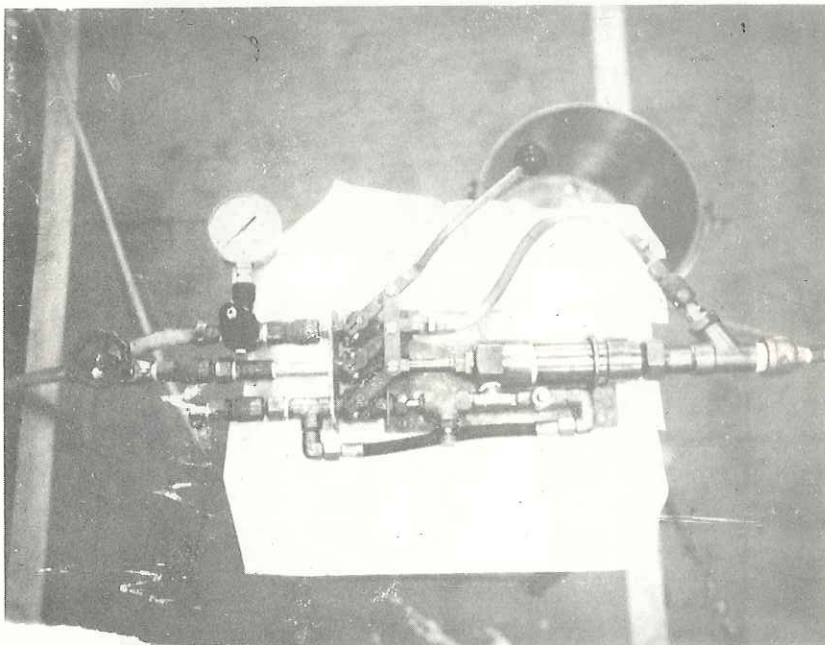


Figure 11. UF Foam Generator Head

90°C was erratic. The ball valves supplied with the machine did not permit precise enough control of the flow of the several ingredients through the nozzle. The flow of resin was either too great, resulting in a creamy liquid product, or too small, resulting in gas blow-by and a sputtering discharge.

A Hoke needle valve was installed in the gelatin solution supply line for better flow control. Then, 20% gelatin solution containing 1.5% Hi-Ex was processed.

The tank containing the gelatin solution was pressurized to 60 pounds and the needle valve controlling the flow of gelatin was wide open. The air pressure to the nozzle was set at 60 psi and the rate of air flow adjusted to produce a good frothy foam. The foam that was produced had a density of 7.25 lb/ft². It took 3 to 4 days to set up and dry completely. This was too long a time to be practical for our purposes.

Attempts were made to improve the early strength of the gelatin froth foam by adding glutaraldehyde to the foam stream. This reagent reacts with the gelatin to crosslink it thereby making it insoluble, and increasing the molecular weight. However, at the high temperatures (60-80°C) required to produce a gelatin solution with a sprayable viscosity, reaction with the glutaraldehyde solution was much too rapid, and crosslinking and gelation occurred in the nozzle necessitating complete disassembly of the nozzle.

The direct spraying of gelatin froth foams using a UPC generator did not appear to be a practical means of producing foams when compared with the early results achieved with the Oakes mixer.

b. Urea/Formaldehyde Foams

A quantity of urea/formaldehyde foam was produced using commercial foam materials supplied by the Rapco Company. These foams had a dry density of 0.5 to 0.7 lb/cu ft. They would probably be suitable for packaging very light weight items.

With eventual disposal of the used foam in mind, several tests were conducted to evaluate the UF foam's resistance to mechanical breakup, chemical attack, and possible microbial degradation. The results were as follows:

- . Pieces of foam were placed in water and stirred at low speed in a Waring Blendor. The foam broke up quickly into fine uniform particles that all floated to the surface. This is probably more violent agitation than would be encountered in any natural disposal procedure.

Pieces of foam were placed in water and stirred at moderate speed using a magnetic stirring bar.

The foam broke up, but quite slowly. The original chunks (approximately 1 to 2 inches in diameter) were still not completely broken up after 8 hours of agitation in water. This form of agitation would simulate somewhat the disposal of the foam directly into the sea.

Pieces of foam were placed in open jars containing the following solutions. The only agitation occurred when the jar was moved during examination to observe the effects of the exposure. These samples were evaluated over an 11-day period.

- Water containing 5% (by weight) of concentrated H_2SO_4 solution: little visible change; foam still afloat; no appreciable break up.
- Water containing 5% (by weight) of NaOH: pieces floated low in the solution; they appeared saturated; there was some break up.
- Water (ordinary tap water): pieces floated high in water; they appeared reasonably dry (not saturated); there was no appreciable break up.

There was no evidence of mold (fungus) or bacterial growth during the first 2 weeks of the test. These samples were retained and observed for several additional weeks. After 3 weeks total time, small clusters of a pink mold was observed on one of four samples being tested. This mold grew slowly and after 4 weeks the foam began to break up. There is not sufficient evidence to warrant saying this foam is generally biodegradable.

The resistance of the UF foam to normal mechanical breakup, chemical attack, or biodegradation emphasized the necessity of incorporating some ingredients into the foam to facilitate its breakup and disposal.

c. Urea/Formaldehyde Foam Containing Gelatin
or Polyvinyl Alcohol

Another avenue of investigation was the possible incorporation of gelatin or polyvinyl alcohol into the urea/formaldehyde foam. The technique to make urea/formaldehyde foam is already well established, and produces a poured-in-place foam which has many attractive properties for this application. Our purpose in introducing gelatin or polyvinyl alcohol into the urea/formaldehyde foam, was to introduce a water-soluble phase into the foam structure. It was hoped that this would facilitate the disintegration of the foam.

Dissolving of gelatin (in granular form) directly into the urea/formaldehyde resin solution with warming and stirring was attempted. It was found that crosslinking of the resin occurred before any appreciable quantity of gelatin was dissolved.

Previously prepared gelatin solution was found to be compatible with the resin solution when gradually added with stirring and warming. However, when the concentration of gelatin exceeded approximately 5 parts per 100 parts of UF resin solution, the viscosity of the resin solution increased markedly. This viscosity increase was due to the reaction of the gelatin and UF resin. It would complicate the spraying of the UF foam and also probably shorten the pot life of the UF/gelatin solution.

An attempt to mix the gelatin solution with the UF foaming agent (aqueous solution of a surfactant and an acidic catalyst) showed them to be incompatible. The gelatin precipitated out of solution, forming a sticky, viscous mass immediately after the gelatin solution was added to the foaming solution.

Because of the incompatibility of the gelatin with the urea/formaldehyde reactants, it was necessary to prepare this resin in the conventional manner and then introduce the hot (60°C) gelatin solution just downstream from the mixing chamber, where the prepolymer mixes with the foaming agent/catalyst

froth. Flow rates for both the urea/formaldehyde resin reactants and for the gelatin solution through the valves and nozzles were determined. The flow rates were controlled so that foams containing 5 and 10% gelatin were prepared.

Using the same techniques, foams were prepared which contained 5 and 10% polyvinyl alcohol (Gelvatol 1-30).

Both the UF/gelatin and the UF/polyvinyl alcohol foams appeared very similar to conventional urea/formaldehyde foams. The compressive strengths of these foams, along with that of unmodified urea/formaldehyde foam, were determined. There was no significant difference in strength between these foams. These modified foams were tested for durability in water. There did not appear to be any significant difference in their durability in water compared to that of the unmodified foam. The use of gelatin and/or polyvinyl alcohol thus did not appear to offer any improvement in performance over that experienced with urea/formaldehyde foam.

2.3.5.3 Miscellaneous Methods

a. Flotation Process

Gaseous nitrogen was evaluated as a blowing agent. An apparatus was set up using a funnel with a fritted glass bottom. The funnel was connected directly to the cylinder

of nitrogen. A thin layer of 25% gelatin solution containing 1.5% Hi-Ex was spread onto the glass bottom of the funnel. The solution temperature was 55-60°C. Nitrogen was blown through the solution at 2 psig. Frothed foam was produced.

This apparatus was modified by installing a metal pan below the funnel for collecting the foam that overflowed from the funnel. Three samples were foamed. The first sample was a 35% gelatin solution. The second was 35% gelatin solution plus Hi-Ex. The third was 35% gelatin solution plus Hi-Ex and aluminum silicate. All the foamed gelatin samples had very uneven cell size and collapsed easily.

As a continuation of this work, foams were formed using Vazo, a thermally unstable compound which produces nitrogen in situ when heated. Gelatin solutions (35%) containing this compound were heated in an oven at 100°C. Brittle foams were produced by this method. They did not appear promising as a packaging material.

b. Gelatin/Ethylene Glycol Solutions

Gelatin/glycol solutions (25/75% by volume) were prepared. This material remained rubbery and viscous after standing for 24 hours. It could be foamed in a vacuum oven at 100°C, but the foams collapsed as soon as the vacuum was removed. This was probably due to the plasticization of gelatin by ethylene glycol.

In another series of experiments, a Fisher-Johns Melting Point Apparatus was used as a heating element. A segment of Plexiglas pipe of approximately 1.5 inches I.D. was used as the vacuum/heat chamber. This pipe was sealed around the heating stage of the apparatus, and vacuum was applied. Control was achieved with a needle valve and a manometer.

A 42% gelatin solution was prepared and divided into four equal portions. Ethylene glycol was added to three of them in the amounts of 2.5 grams, 5 grams, and 10 grams, respectively. The solution was allowed to cool and gel. Small samples of these gels were put in the Plexiglas chamber. When the heating temperature reached 75-80°C, the samples started to foam and did not collapse on standing. When the temperature reached 110°C, the samples foamed very well. However, more cells and larger cells were formed and the foam bubbles began to burst. The presence of ethylene glycol rendered the foam rubbery. The higher the glycol concentration in the sample, the more rubbery the texture of the foam.

c. Production of Foam Beads Using Spray Drying Technique

Late in the program, preliminary experiments were made to produce foamed beads using a spray drying technique. Gelatin solutions (15%) containing 1.5% Vazo were sprayed into the

top of a column through which heated air (100-120°C) was blown. It was hoped that the heated air would rapidly evaporate the water from the droplets and decompose the Vazo to blow the drop into a foam bead. The heat output of the heat guns was not great enough to evaporate the water from the relatively large drops and to decompose the Vazo. A very small number of foam beads were produced. Sufficient time was not available to fully develop this process.

d. Foams Produced From Gelled Solutions

A gelatin solution (25%) was prepared using conventional techniques. The solution contained 1.5% Hi-Ex foaming agent. One liter of this solution was prepared.

Nine 100-cc samples were measured out separately, and each sample was put in a small beaker. To each of the first three samples, glass microballoons were added in the amounts of 0.5 cc, 1.0 cc and 1.5 cc, respectively. Similarly, three samples containing like amounts of aluminum silicate and carbon black were also prepared.

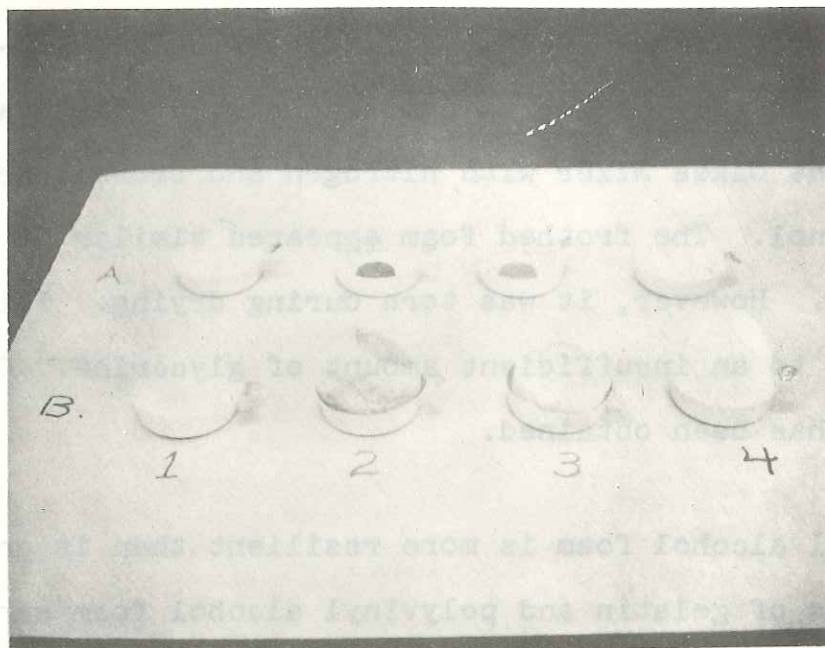
Each of these nine samples was reheated to 40°C and 1.5 grams of ammonium carbonate $[(\text{NH}_4)_2\text{CO}_3]$ were then added to each sample.

The samples were then poured onto a stainless steel cold plate to form discs of gelled material. Small pieces of each of these were then cut off and placed separately in aluminum dishes. These were put in a vacuum oven. Through use of a series of temperature/vacuum combinations, it was found that the most favorable condition for foaming these samples was 27 inches of vacuum at 50°C. This experiment was repeated with 35% gelatin solution with better results (Figure 12.) However, the cell size of these foamed samples was large and the foam strength was low.

2.4 NON-AQUEOUS SOLVENT-BLOWN FOAMS

Two samples of a non-aqueous system were prepared in one-pint glass pressure bottles. The first sample was a mixture of gelatin and ethylene oxide gas; the second was a mixture of gelatin, ethylene oxide, and methanol. They were allowed to mix for 72 hours. Both of these samples were under gas pressure at room temperature (~7 psi).

The bottles were then cooled in dry ice and opened. Pieces of solvent-swollen gelatin were placed in an oven at 100°C. As the temperature of the gelatin rose, foaming from internal pressure resulted. The foam obtained from the sample containing both ethylene oxide and methanol was the better of the two preparations.



- 1) 0.5 cc $\text{Al}_2(\text{SiO}_4)_3$
- 2) 1.5 cc Carbon Black
- 3) 0.5 cc Carbon Black
- 4) 1.5 cc Glass Microballoons
- A) Before Vacuum Heating
- B) After Vacuum Heating

Figure 12. Side View of Foamed-Up Samples

This was a very preliminary experiment but appears to indicate a way to make bead foams using non-aqueous systems.

2.5 OTHER WATER-SOLUBLE POLYMERS

Besides gelatin, preliminary studies were conducted on three other water-soluble polymers. Promising results were obtained using polyvinyl alcohol (Gelvato1 1-30). A Gelvato1 1-30 (20%) glycerine (20%) solution containing 1.5% H1-Ex was frothed in the Oakes Mixer with nitrogen and crosslinked with resorcinol. The frothed foam appeared similar to gelatin foam. However, it was torn during drying. This was probably due to an insufficient amount of glycerine. One good sample has been obtained.

The polyvinyl alcohol foam is more resilient than is gelatin foam. Pieces of gelatin and polyvinyl alcohol foam were compressed to approximately 25% of their original thickness and kept in this condition for seventeen hours. At the end of this time the weight was removed and the thickness of the foam was measured immediately and after 5 minutes and 1 hour. Table 4 summarizes this work. Gelatin foam did **not recover after** compression, while polyvinyl alcohol quickly recovered 67% of its original thickness and after 1 hour recovery reached 90% of the original thickness.

Table 5

COMPRESSION PROPERTIES OF GELATIN AND POLYVINYL ALCOHOL FOAMS

<u>Condition</u>	<u>Gelatin Foam</u>		<u>Polyvinyl Alcohol</u>	
	<u>thickness (in.)</u>	<u>%</u>	<u>thickness (in.)</u>	<u>%</u>
Original	1-1/8	100	1-1/8	100
After adding weight	1/4	22	5/16	27.8
After 17 hours (immediately after weight was removed)	1/4	22	3/4	66.7
Five minutes after weight was removed	1/4	22	15/16	83.3
One hour after weight was removed	1/4	22	1	88.9

Polyvinyl alcohol foam has a material cost of \$0.94/lb while gelatin foam costs \$2.33/lb.

The setting time for polyvinyl alcohol foam crosslinked with resorcinol is the same as for gelatin foam.

Two polyvinyl pyrrolidone polymers (PVP K-15 and PVP K-30) were evaluated. Both polymers could be made into 60% solution and foamed by adding $(\text{NH}_4)_2\text{CO}_3$ and heating. However, the foam collapsed on standing. An attempt was also made to blend gelatin with the PVP polymer without positive results.

AP-250, an acrylonitrile/methyl vinyl pyridine copolymer was also evaluated. It could not be made into a high-concentration solution. At 20% concentration, only a highly viscous sludge was produced. Therefore, no foaming study was made on this polymer.

Experiments were also carried out to evaluate the blending of urea/formaldehyde foam with water-soluble foam. Although urea/formaldehyde foam is a well-established product, it is insoluble in water and resistant to mechanical breakup and chemical attack. It was conceived that gelatin, when homogeneously dispersed throughout the urea/formaldehyde foam, might act as a weak (water-soluble) link in the chain that would facilitate the physical breakup of the foam in water. UF/gelatin foam samples were prepared using a UF foam generator and put in water in a beaker. The samples became very water-logged and sank to the bottom of the beaker, but did not completely break up. This work is reported in Section 2.3.4.2.

UF/polyvinyl alcohol foam samples were also prepared with the UF foam generator and soaked in water. The same result was obtained.

3. CONCLUSIONS

- a. Gelatin solutions containing 10 to 40% gelatin could be processed into foam in an Oakes Mixer, using either Ucon 12 or Hi-Ex/nitrogen as frothing agent. The Ucon 12-frothed gelatin foam had very uneven cell size, but very uniform fine cell foam was produced by Hi-Ex/nitrogen frothing. This froth foam could be applied by pour-in-place method or could be made into blocks. Alternatively, it could be spread onto kraft paper in rod form and later cut into

"pillows". The density of the blocks could be as low as 1.24 lb/cu ft. The lowest bulk density of the "pillows" was 0.77 lb/cu ft. The material cost of gelatin foam is \$2.33/lb.

- b. To help maintain the moisture content in gelatin foam, glycerine was employed as a humectant added to the gelatin solution in the weight proportion of 2/1 gelatin/glycerine. During the preparation of gelatin/glycerine solution, water and glycerine were mixed and heated, and the gelatin was then stirred in the water/glycerine mixture. Gelatin (30 to 40%)/glycerine (15 to 20%) solutions, could be prepared without difficulty in this way.
- c. Polyvinyl alcohol solution could also be frothed into foam in the Oakes Mixer by the process similar to that used for gelatin. However, only preliminary work on this material was done. More work is required to develop this foam more fully. Polyvinyl alcohol foam has a potential material cost of about \$0.94/lb. It is much more resilient than is gelatin foam.
- d. Urea/formaldehyde foams were made during this program using a commercial foam generator. These foams were made from commercial solutions that are currently sold

to produce insulation-type foams. These foams were also modified by having 5 and 10% of either gelatin or polyvinyl alcohol incorporated into them. Both the straight urea/formaldehyde and the modified foams were tested for resistance to water, dilute acid, and dilute base. None of these foams showed any tendency to disintegrate completely under these conditions even though the test was continued for 3 to 4 weeks. They do not appear to be a good approach to an environmentally degradable packaging material.

4. RECOMMENDATIONS

The following recommendations are made for future work on environmentally degradable foams:

- a) The study of gelatin foams should be continued. Gelatin foam has been successfully produced by frothing gelatin/glycerine solution in an Oakes Mixer. It is recommended that this program be continued with the following three objectives: (1) to improve foam properties by modifying the gelatin foam solution formulation; (2) to reduce the cost of foam; and (3) to develop a practical foaming process as well as a portable foam machine.

- b) Target foam properties should be set up to serve as a reference guide for the improvement of foam quality. At the same time, lower grade gelatin and glycerine (if available) should be evaluated. Surfactants with their compositions similar to that of the main ingredient of Hi-Ex should be evaluated as a possible substitute for this proprietary material.
- c) The preferred procedures for packaging applications envisioned by the Army should be defined. After an adequate foaming process has been developed to meet these needs, a portable foam machine should be designed and fabricated. The accessories should include gelatin solution preparation and storage units, hot water, nitrogen or air, and electricity supply.
- d) During the present study, polyvinyl alcohol foam could also be generated with the Oakes Mixer. However, the samples obtained from the preliminary work tended to tear on standing. This might be due to the fast drying of the foam or to insufficient glycerine or other plasticizer. Since the gelatin foaming process has been well established, it will serve as a basis for further development of foaming processes for polyvinyl alcohol. The

- e) polyvinyl alcohol foams generated to date were much more resilient than were the gelatin foams. Polyvinyl alcohol is also less expensive than gelatin. On this basis alone a considerable effort to develop polyvinyl alcohol foams is indicated.
- f) Efforts should be continued to find other water-soluble polymers that might produce practical environmentally degradable packaging foam.